

# First-principles Calculation of the Formation Energy in MgO–CaO Solid Solutions

S. V. Stolbov<sup>(1)</sup>, R. E. Cohen<sup>(1,2)</sup>

<sup>(1)</sup>*Carnegie Institution of Washington, Washington, DC 20015*

<sup>(2)</sup>*Seismological Laboratory, California Institute of Technology, Pasadena, CA 91125*

The electronic structure and total energy were calculated for ordered and disordered MgO–CaO solid solutions within the multiple scattering theory in real space and the local density approximation. Based on the dependence of the total energy on the unit cell volume the equilibrium lattice parameter and formation energy were determined for different solution compositions. The formation energy of the solid solutions is found to be positive that is in agreement with the experimental phase diagram, which shows a miscibility gap.

## I. INTRODUCTION

In the last decade significant progress was achieved in application of first principles methods to calculate properties of materials. The full-potential linearized-augmented-plane-wave (FLAPW) and ultra-soft pseudopotential methods allow one to map phonon potential surface, describe phase transitions, electromechanical properties of ferroelectrics [1–3] and magnetic properties of materials [4]. However these methods are applicable to ordered systems with translational symmetry, whereas many technologically relevant materials do not meet this requirement. Such important properties as ultrahigh piezoelectric efficiency, colossal magnetoresistance, high oxygen permeation through fuel cell membranes occur only when corresponding oxides form solid solutions, most of which are disordered.

First-principles methods developed for disordered systems are mostly based on the Green’s function formalism such as the Korringa-Kohn-Rostoker (KKR) method [5,6] that allows one to take into account atomic disorder within the average  $t$ -matrix (ATA) [7,8] or

coherent potential (CPA) [9,10] approximations. They have been successfully applied to metallic alloys [11–15]. A few calculations were performed for copper oxides [16,17] with mixed covalence – ionic character of chemical bonding. In the present paper, we consider the simplest oxide solid solution, the system MgO-CaO. Magnesiowüstite (Mg,Fe)O is believed to be a major constituent of the Earth’s lower mantle, so that it would be an ideal system for study, but the FeO constituent leads to complex Mott insulator behavior. The study of CaO in MgO can be considered as a step in the direction of the understanding of solid solution in minerals, as well as important in understanding the behavior of the minor element Ca. Understanding of oxide solid solutions is also important from the perspective of ferroelectric solid solutions and high temperature superconductors.

Several approaches have been used previously to study the MgO-CaO system. The electronic structure and total energy were calculated for constitutive compounds of the system, MgO and CaO using FLAPW method [18]. A potential model [19] was developed to compute the phase diagram of the MgO-CaO solid solution. However the approach was found to be inadequate to reproduce the properties with required accuracy. Authors of Ref. [20] applied a tight-binding method to calculate the formation energy of ordered MgO-CaO solutions. Tight-binding parameters were obtained from results of first principles pseudopotential calculations performed for MgO, CaO and MgCaO<sub>2</sub> compounds and then used for computing the total energy of solutions with different compositions and crystal structures. Comparison with the pseudopotential results suggests that the tight-binding approach is an efficient tool to study ionic oxides. However those were still ordered systems.

In the present paper, we considered both ordered and fully disordered MgO-CaO solutions using the multiple scattering theory within the local density approximation. We calculated the electron structure, total energy, equilibrium lattice parameters and formation energy for ordered MgO, CaO and MgCaO<sub>2</sub> compounds as well as for 4 disordered MgO-CaO solutions with different compositions. The obtained formation energy values were compared to results of Ref. [20].

## II. COMPUTATIONAL METHOD

The calculations were performed by means a computer code based on the local density approximation (LDA) [21] and multiple scattering theory. The code embodies the local self-consistent multiple scattering (LSMS) method [22] where a compound is divided into overlapping clusters – local interaction zones (LIZs) centered around atoms of different sorts. The multiple scattering problem is solved for each LIZ separately in the *lattice site* – *angular momentum* representation for the *muffin-tin* (MT) potential given the cluster Green’s functions, the local densities of electron states and valence charge density for central atom.

Our approach is self-consistent with respect to local charge densities and potentials. However it does not treat the disorder self-consistency. We use an actual single site scattering matrix  $t_l^i(E)$  for the central atom of LIZ and average  $t$ -matrix:  $\tilde{t}_l^i = xt_l^a + (1 - x)t_l^b$  for surrounding sites, if they belong to a sublattice with a substitutional disorder of the  $a$ - and  $b$ -sort atoms with concentrations  $x$  and  $1 - x$ . According to the Ref. [8], such an approach is more accurate than the regular average  $t$ -matrix approximation. In the considered solid solution the Mg and Ca atoms randomly occupy the metal sublattice sites. They have the same number of valence electrons. This also allows us to believe that our approximation is reasonable for the system. One more advantage of the approach is it can be explicitly implemented within the ordinary LSMS theory [22].

Solving the Poisson equation at each iteration, we use the actual charge density for the local contribution to the MT potential and the average charges for the contribution of the substitutionally disordered sublattice to the Madelung potential. The exchange and correlation parts of the potential is determined within LDA using the technique described in Ref. [23].

The total energy was calculated following procedure described in Ref. [12] and using an expression for multicomponent compound [24].

In the present calculations, each LIZ built around Mg, Ca and O sites contained 123

atoms. This provided good convergence over the LIZ size, since the difference in the total energies obtained for 123 and 93 atom LIZs was 3 and 5 mRy for MgO and CaO respectively. To estimate an error induced by MT potentials, the calculations were performed in two approximations – maximum MT radii proportional to the unit cell volume and fixed MT radii corresponding to a minimum volume considered for a given compound.

### III. RESULTS AND DISCUSSION

The density of electron states, charge density and total energy were calculated versus the unit cell volume for ordered compounds MgO, CaO and MgCaO<sub>2</sub> and disordered solid solutions Mg<sub>1-x</sub>Ca<sub>x</sub>O with  $x = 0.2, 0.5, 0.7, 0.8$ . For MgCaO<sub>2</sub> the structure was chosen where cations were ordered by an alternate stacking of Mg and Ca planes along the [001] direction. Thus the cations form the Ll<sub>0</sub> structure in Strukturbericht notation [25].

Based on the computed volume dependence of the total energy the equilibrium volumes were calculated for each considered compound. The results are shown in Fig. 1. The concentration dependence of unit cell volume is found to be close to linear one, though some wavy behavior is seen. The difference in results obtained by means of maximum and fixed MT radii approaches gives an order of magnitude for the error induced by *muffin-tin* approximation. For the MgO and CaO compounds the calculated equilibrium volumes are less than experimental ones that reflects the well known feature of LDA.

Using the calculated values of total energy we have determined the formation energy of the solutions determined as:

$$E_f = E(Mg_{1-x}Ca_xO) - [(1-x)E(MgO) + xE(CaO)],$$

where E is the total energy of corresponding compound. The  $E_f$  values compared to results of pseudopotential calculations [20] are shown in Fig. 2. Our result and result of Ref. [20] obtained for the ordered Ll<sub>0</sub> phase of MgCaO<sub>2</sub> are in a good quantitative agreement (0.285 eV and 0.282 eV respectively). The difference in formation energy of the ordered and

disordered  $\text{MgCaO}_2$  is less than 10%. Such a small difference takes place since a decay of band states caused by random potentials mostly involves unoccupied states in these ionic compounds and is much lower than in case of materials with covalence bonding [17]. The formation energy is found to be positive for all considered solid solutions suggesting that a phase separation is preferable for this system. This is in agreement with the experimental phase diagram [26], which shows a miscibility gap.

Charge transfer is one of the key mechanisms determining the total energy of complex oxides. Therefore, we have calculated effective charges on atoms in the considered solid solutions by integration of the valence electron density over Wigner-Seitz spheres. It is important at this stage to make a clear reasonable definition of the space belonging each nonequivalent atom that is determined by the ratio of the Wigner-Seitz radii  $r_O^{WS}/r_M^{WS}$  (subscripts  $O$  and  $M$  denote oxygen and metal respectively). We suppose that in the present case it is convenient for interpretation purpose to keep this ratio independent of the metal composition. This ratio should also make some physical sense. Because the considered solutions are definitely ionic, the ratio should be related to the ionic radii. Thus we come to the Wigner-Seitz radii ratio defined as

$$r_O^{WS}/r_M^{WS} = 2R_i^{OII}/[R_i^{MgII} + R_i^{CaII}] = 1.24,$$

where  $R_i^{OII}$ ,  $R_i^{MgII}$  and  $R_i^{CaII}$  are ionic radii of O, Mg and Ca respectively. We have also determined the average cation charges in the solutions as  $Q_{av} = (1 - x)Q_{Mg} + xQ_{Ca}$ . The results are shown in Fig. 3. Since the Ca atom has the valence wave functions more extended than Mg, substitution of Mg with Ca leads to a noticeable increase in the electron charge on oxygen atoms (more than 0.2e, going from MgO to CaO). The concentration dependence of these charges as well as average cation charges are found to be linear.

In summary, we have calculated the electron structure, total energy, equilibrium lattice constants and formation energy for ordered and disordered solid solutions  $\text{Mg}_{1-x}\text{Ca}_x\text{O}$ . A linear composition dependence has been found for lattice parameters and effective charges. The formation energy is positive for all considered materials that is in agreement with the

experimental phase diagram. The results suggest that LSMS method and LDA can be an efficient tool to study properties of disordered ionic solutions.

**Acknowledgements.** This work was supported by Office of Naval Research grant N00014-97-1-0052. Computations were performed on the Cray SV1 at the Geophysical Laboratory, supported by NSF grant EAR-9975753 and the W. M. Keck Foundation.

---

- [1] R. E. Cohen, *Nature* **358**, 136 (1992).
- [2] H. Fu and R. E. Cohen, *Nature* **403**, 281 (2000).
- [3] R. D. King-Smith and David Vanderbilt *Ferroelectrics* **136**, 85 (1992).
- [4] D. J. Singh, *Phys. Rev. B* **55**, 313 (1997).
- [5] J. Korringa, *Physica* **13**, 392 (1947).
- [6] W. Kohn and N. Rostoker, *Phys. Rev.* **94**, 1111 (1954).
- [7] H. Ehrenreich and L. M. Schwartz, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1976), Vol. 31.
- [8] A. Bansil, *Phys. Rev. B* **20**, 4025 (1979).
- [9] P. Soven, *Phys. Rev.* **156**, 809 (1967).
- [10] D. W. Taylor, *Phys. Rev.* **156**, 1017 (1968).
- [11] D. D. Johnson, D. M. Nicholson, F. J. Pinski, B. L. Gyorffy, and G. M. Stocks, *Phys. Rev. Lett.* **56**, 2088 (1986).
- [12] D. D. Johnson, D. M. Nicholson, F. J. Pinski, B. L. Gyorffy, and G. M. Stocks, *Phys. Rev. B* **41**, 9701 (1990).
- [13] F. J. Pinski, B. Ginatempo, D. D. Johnson, J. B. Staunton, G. M. Stocks, and B. L. Gyorffy,

- Phys. Rev. Lett.* **66**, 766 (1991).
- [14] R. G. Jordan, Y. Liu, S. L. Qiu, B. Ginatempo, E. Bruno, G. M. Stocks, and W. A. Shelton, *Phys. Rev. B* **50**, 11459 (1994).
- [15] I. A. Abrikosov and B. Johansson, *Phys. Rev. B* **57**, 14164 (1998).
- [16] L. Szunyogh, P. Weinberger, and R. Podloucky, *Phys. Rev. B* **43**, 519 (1991).
- [17] S. V. Stolbov, *Solid State Commun.* **94**, 451 (1995)
- [18] M. J. Mehl, R. E. Cohen, and H. Krakauer, *J. Geophys. Res.* **93**, 8009 (1988).
- [19] P. D. Tepesch, A. F. Kohan, G. D. Garbulsky, G. Ceder, C. Coley, H. T. Stocks, L. L. Boyer, M. J. Mehl, B. P. Burton, K. Cho, and J. Joannopoulos, *J. Am. Ceram. Soc.* **79**, 2033 (1996).
- [20] A. F. Kohan, G. Ceder, *Phys. Rev. B* **54**, 805 (1996).
- [21] W. Kohn, L. J. Sham, *Phys. Rev.* **140**, 1133 (1965).
- [22] Y. Wang, G. M. Stocks, W. A. Shelton, D. M. C. Nicholson, Z. Szotek, W. M. Temmerman, *Phys. Rev. Lett.* **75**, 2867 (1995).
- [23] O. Gunnarsson, B. I. Lundqvist, *Phys. Rev. B* **13**, 4274 (1976).
- [24] P. C. Schmidt, *Phys. Rev. B* **31**, 5015 (1985).
- [25] T. I. U. of Crystallography, *International Tables for Crystallography* (Kluwer Academic, Dordrecht, 1989).
- [26] Y. Yin and B. B. Argent, *J. Phase Equilibria* **14**, 588 (1993).

FIG. 1. The composition dependence of the equilibrium volume per oxygen atom calculated with maximum MT radii (squares) and fixed MT radii (circles). The dot-dashed line connects the experimental volume values obtained for stoichiometric MgO and CaO compounds.

FIG. 2. The formation energies calculated in the present work for disordered  $\text{Mg}_{1-x}\text{Ca}_x\text{O}$  solid solutions (triangles), ordered  $\text{MgCaO}_2$  compound (circle), as well as obtained by means of pseudopotential method [20] for the following ordered phases:  $x = 0.25$  ( $\text{CaMg}_3\text{O}_4$ ), higher cross -  $Ll_2$  structure, lower cross -  $DO_{22}$  structure;  $x = 0.33$  ( $\text{CaMg}_2\text{O}_3$ ) -  $\text{MoPt}_2$  structure;  $x = 0.5$  ( $\text{CaMgO}_2$ ), from higher to lower cross -  $Ll_0$ ,  $Ll_1$  and  $A_2B_2$  structures respectively;  $x = 0.67$  ( $\text{Ca}_2\text{MgO}_3$ ) -  $\text{MoPt}_2$  structure;  $x = 0.75$  ( $\text{Ca}_3\text{MgO}_4$ ) higher cross -  $Ll_2$  structure, lower cross -  $DO_{22}$  structure;  $x = 0.8$  ( $\text{Ca}_4\text{MgO}_5$ ) -  $\text{Ni}_4\text{Mo}$  structure.

FIG. 3. The composition dependence of Wigner-Seitz charges on Mg (up triangles), Ca (down triangles), O (circles) and average cation charges (squares) in  $\text{Mg}_{1-x}\text{Ca}_x\text{O}$ .







